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Heck Arylation of Acrylonitrile with Aryl Iodides Catalyzed by a Silica-bound Arsine Palladium(0) Complex

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Abstract: Acrylonitrile reacts with aryl iodides in the presence of tri-*n*-butylamine and a catalytic amount of a silica-bound arsine palladium(0) complex to afford stereoselectively (E)-cinnamonitriles in high yields.

Keywords: Polymeric palladium catalyst, Heck arylation, (E)-cinnamonitrile, arsine palladium(0) complex, stereoselective synthesis.

The palladium-catalyzed arylation of alkenes is an important discovery in organopalladium chemistry made by Heck *et al.* and has found wide application in organic synthesis[1,2]. In this reaction, homogeneous palladium complexes such as $Pd(OAc)_2$ are usually used as the catalysts and the amount of catalyst used is about 2 mol% of reactant. Although homogeneous palladium catalysts have proven to be efficient, their activity and stereoselectivity are moderate and use of homogeneous palladium catalysts is still expensive for large scale preparation. Polymer-supported organotransition metal complexes catalysts offer several significant advantages in synthetic and industrial chemistry and are currently attracting great interest. Polymer-supported phosphine palladium, sulfur palladium complexes catalysts have been successfully used for a variety of organic reactions[3-9]. Choudary *et al.*[4] described a clay anchored phosphine palladium complex catalyzed arylation of acrylonitrile with iodobenzene, but no procedure to recover the catalyst was detailed. Study of new types of polymer-bound palladium catalysts which might be suitable for Heck arylation of conjugated alkenes has theoretical and practical significance.

Cinnamonitriles are important synthetic intermediates and more attention has been given to the stereoselective synthesis of (E) and (Z)-cinnamonitriles in recent years. Huang *et al.*[10] reported that (Z)-cinnamonitriles were prepared in 78-98% yields by the desulfonylation of α-phenylsulfonylcinnamonitriles in the presence of NaHTe. Guo and Zhang[11] found that (E)-cinnamonitriles could be obtained in 68-85% yields by a procedure of reduction of α-phenylsulfonylcinnamonitriles with SmI_2 in THF-MeOH solution. Although these methods have provided useful routes for stereoselective

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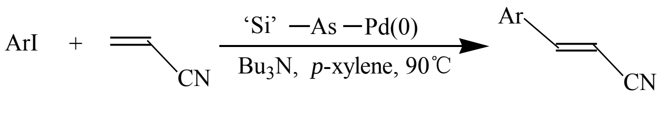
synthesis of (E) and (Z)-cinnamonitriles, sometimes the α-phenylsulfonylcinnamonitriles are not readily available. A convenient alternative technical synthesis of (E)-cinnamonitriles is the Heck arylation of aryl iodides with acrylonitrile, the homogeneous palladium complexes such as $Pd(OAc)_2$ or $Pd(PPh_3)_2Cl_2$ are usually used as the catalysts in the arylation reaction[12,13]. As Heck[14] has noted, practical application of the reaction under such conditions is not feasible due to its expensive cost. Recently, we have found that the silica-bound arsine palladium(0) complex ('Si'-As-Pd(0)) is a highly active catalyst for arylation of styrene and acrylic acid with aryl halides[15]. In this paper, we wish to report that (E)-cinnamonitriles could be synthesized stereoselectively in high yields *via* Heck arylation of acrylonitrile with aryl iodides catalyzed by a silica-bound arsine palladium(0) complex (**Scheme 1**).

Treatment of iodobenzene (2 mmol) with acrylonitrile (4 mmol) in *p*-xylene (0.3 mL) at 90℃ for 6 h in the presence of 'Si'-As-Pd(0) (0.01 mmol), Bu_3N (2.2 mmol) afforded (E)-cinnamonitrile in 88% yield. We applied the reaction to various substituted iodobenzenes, typical results are showed in **Table 1**. As seen from the **Table 1**, the arylation reactions of acrylonitrile with substituted iodobenzenes also proceeded smoothly and a variety of substituted (E)-cinnamonitriles were obtained in high yields. The arylation reaction can tolerate a variety of functional groups on the aryl iodides, both strongly electron donating and withdrawing substituents can be present. This polymeric palladium(0) catalyst is stable to air and moisture and can be easily recovered by simple filtration. The catalytic activity of the recovered catalyst was tested for arylation of acrylonitrile with 4-chloroiodobenzene for three recycle, and it was found that the yield of (E)-4-chlorocinnamonitrile decreased by 2%, 1% and 2% in each recycle, respectively.

Scheme 1



1 **2** **3**

Table 1 Synthesis of (E)-cinnamonitriles **3a-g** according to **Scheme 1**

Entry	ArI	Mp/℃(lit)	Product[a]	Yield[b](%)
1	C_6H_5I		**3a**	88
2	$4\text{-}CH_3C_6H_4I$	69-70(70-71)[16]	**3b**	90
3	$4\text{-}CH_3OC_6H_4I$	62-63(64)[16]	**3c**	93
4	$4\text{-}ClC_6H_4I$	82-83(84-85)[16]	**3d**	95
5	$4\text{-}O_2NC_6H_4I$	198-199(200)[16]	**3e**	89
6	$3\text{-}O_2NC_6H_4I$	157-158(159)[16]	**3f**	91
7	$4\text{-}CH_3OCOC_6H_4I$	144-145(143-145)[17]	**3g**	92

[a] All the compounds were characterized by IR、^1H NMR.

[b] Isolated yield based on the aryl iodide **1** used.

Investigations of the crude products **3** by ^{1}H NMR spectroscopy (300 MHz) showed their isomeric purities of more than 98%, the *trans*-selectivity was near quantitative. The stereochemistry of the products **3** was easily established, since the spectra of products **3** give rise to a doublet at δ 5.43-6.24 with coupling constant of J = 16.0-16.7 Hz, typical of *trans* positioned protons.

In conclusion, we have developed a novel approach to the (E)-cinnamonitriles *via* Heck arylation reaction of acrylonitrile with aryl iodides catalyzed by a silica-bound arsine palladium(0) complex. The present method for preparing (E)-cinnamonitriles has the advantages of being a simple and practical procedure, carried out under mild reaction conditions and giving high yields.

Experimental

The silica-bound arsine palladium(0) complex ('Si'-As-Pd(0)) was prepared according to the literature procedure[15], the arsenium and palladium content was 1.40 mmol/g and 0.39 mmol/g, respectively. Melting points were taken with a Yanoco micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC-P300 (300 MHz) spectrometer with TMS as an internal standard (δ in ppm). IR spectra were obtained on a Perkin-Elmer 683 instrument. Bu_3N and *p*-xylene were distilled before use.

*General procedure for the synthesis of (E)-cinnamonitriles **3a-3g***

A mixture of acrylonitrile (4 mmol), aryl iodide (2 mmol), Bu_3N (2.2 mmol), *p*-xylene (0.3 mL) and the 'Si'-As-Pd(0) catalyst (0.01 mmol) was stirred under N_2 in an oil bath at 90 ℃ for 6 h. The mixture was cooled and dissolved in Et_2O (30 mL). The 'Si'-As-Pd(0) catalyst was separated from the mixture by filtration, washed with distilled water (2×10 mL), EtOH (3×10 mL) and Et_2O (3×10 mL) and reused in the next run. The ethereal solution was washed with 5 mol/L HCl (2×10 mL), water (3×10 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel eluting with light petroleum-ethyl acetate (9:1).

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